STUDY THE ELECTRICAL PROPERTIES AND AC CONDUCTIVITY OF PURE PMMA AND PMMA DOPED WITH AZO DYE

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ABSTRACT

Dielectric analysis was performed on pristine and azo-dye doped PMMA with different doping levels. The temperature and frequency dependences of dielectric permittivity (ε'), dissipation factor ($tan\ \delta$) and Ac conductivity (σ_{AC}) are studied in the frequency range 100 Hz -100 kHz in temperature range 30-120 ^{o}C. It is noticed that the values of ε' decreases with increasing frequency and reach to a nearly constant value at high frequency. On the other hand the dependence of ε' on the temperature shows increases of ε' with the temperature up to T_g. The values of $tan\ \delta$ and peak position of pure PMMA are greater than that for the azo dye doped samples. AC conductivity values σ_{AC} for the present system are calculated from the dielectric data while σ_{AC} values increase with increasing the frequency as well as azo dye content. For all investigated samples, at constant temperature, the frequency dependence of σ_{AC} is found to obey the relation $\sigma_{AC} = A\omega^s$. The results show that the correlated barrier hopping mechanism (CBH) is the most suitable mechanism to describe the Ac conduction

KEYWORDS: PMMA; Azo Dye Doping; AC Conductivity, Dielectric Constant

INTRODUCTION

In recent years dye doped polymers have attracted the attention of materials researchers, because the optical and electrical properties can be modified to a specification requirement by doping process. Doping the polymers allows one to creat a new material having some of the desired properties. Azo dyes doped polymers have been investigated extensively in the past decade due to their interesting properties such as the potential application in nonlinear optics, optical storage, optical communication and information processing , especially all optical modulators [1]. Nonlinear optical (NLO) polymers incorporating in azo dyes are candidates for application in optoelectronics because of high flexibility, comptability and ease of production [2]. Optical phenomena in azo dye doped polymers has recently become of special interest in view of the application in photonics [3].

In all disordered materials, the allowed energy bands are not sharp, but have band tails into the mobility gap [4]. The exponential absorption edge, also known as the Urbach edge is an important parameter for characterizing amorphous material and has implications for performance of electronic devices. The optical absorption spectra of many types of polymer has been reported [5-7], but to our knowledge a little attention has been paid to study the optical constants (refractive and absorption indices). Refractive index is an important optical parameter for the design of prisms and optical fibers [8].

Dielectric analysis was performed on pristine and UV-irradiated films of pure PMMA and PMMA doped with different contents of azo dye. The temperature and frequency dependence of dielectric permittivity (ε'), dissipation factor (tan δ) and Ac conductivity (σ_{Ac}) is studied in the frequency range 100 Hz - 100 kHz and temperature range 30-150 ^{o}C. It is noticed that the values of ε' decrease with increasing frequency and reach to constant value at high frequency. On the other hand the dependence of ε' on the temperature shows two regions around the glass transition (Tg). In the low temperature region ε' increases with the temperature, while it decreases in the high temperature region. The results show that the dielectric loss tangent as a function of temperature displays a single peak corresponding to the α-transition (glass transition). The values of tan δ peak of pure PMMA are greater than that for the azo dye doped samples. From the values of tan δ, the activation energy can be calculated and it is found that the value for azo dye doped samples less than that of pure PMMA and decreases with increasing doping level. The Ac conductivity values σ_{Ac} for the present system are calculated from the dielectric data. The σ_{Ac} values increase with increasing the frequency as well as azo dye content. For all investigated samples, at constant temperature, the frequency dependence of σ_{Ac} is found to obey the relation $\sigma_{Ac} = A\omega s$. The results show that the correlated barrier hopping mechanism (CBH) is the most suitable mechanism to describe the Ac conduction behavior in the present system in the frequency range 0.1-100 kHz and temperature range 30-100 ^{o}C.

EXPERIMENTAL PROCEDURE

Samples Preparation

The PMMA poly (methyl methacrylate) used in this work was supplied by Aldrich Chemical, CO, USA and the azo dye is prepared in the laboratory. The present PMMA films doped with different amounts of azo dye were prepared by the casting method as follow: PMMA was dissolved in chloroform for about two days at room temperature. Azo dye was dissolved in chloroform also and added to the polymeric solution. The solutions were left to reach a suitable viscosity. The mixture was casted in glass dishes and kept in a dry atmosphere at room temperature for two weeks to ensure the removal of the solvent traces. The thickness of the obtained films is in the range $0.1 - 0.2$ mm. PMMA films doped with mass fractions 0%, 0.25%, 0.50%, 0.75% and 1% ofazo dye were prepared. The dopant concentration W (wt %) is calculated from the equation :

$$W(wt\%) = \frac{W_f}{W_p + W_f} \times 100, \tag{1}$$

where W_p and W_f represent the weight of polymer and dopant, respectively. The molecular structure of PMMA and azo dye are shown as

Poly (Methyl Methacrylate) (PMMA)   (1-Phenylazo-2-Naphthol) (Azo Dye)
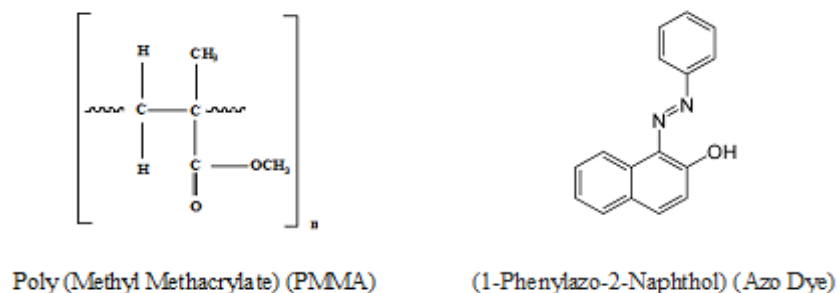
Figure 1

PHYSICAL MEASUREMENTS

The dielectric properties of all samples were measured using a frequency analyzer in the frequency range 100 Hz–100 KHz. A simple circuit is used for our system.

The parallel equivalent circuit mode calculations were selected because of the relatively high impedance and low capacitance of the samples, since parallel resistance can cause great loss in this case. Phase difference (φ) and gain (G) data are measured using a computer program. Data are recorded with increasing the sample's temperature, using temperature controller with different frequencies at each five temperature degrees.

The dielectric parameters which are measured have been calculated from phase difference and gain data using the following equations:

$$G = R^{-1}[r^{-1} + i\omega C_p]^{-1} \qquad (2-1)$$

where G is the gain ratio. Also G can be written as

$$G = \sin \delta / \omega C_p R , \qquad (2-2)$$

where δ is the loss angle has the value:

$$\delta = \tan^{-1}(\omega C_p r), \qquad (2-3)$$

where r is the internal resistance of the sample which causing the loss factor, and was calculated from the measured phase difference data using $\delta = 90 - \varphi$. So,

$$C_p = \sin \delta / \omega GR \qquad (2-4)$$

Dielectric constant (permittivity) έ calculated from the capacitance Cp where:

$$\varepsilon' = C_p C_o d / A \qquad (2-5)$$

where Co is the capacitance at free space, d is the thickness of the sample, A is the cross sectional area of the investigated samples.

The dielectric loss ε" was calculated from the relation:

$$\varepsilon'' = \varepsilon' \tan \delta \qquad (2-6)$$

RESULTS AND DISCUSSIONS

Variation of Dielectric Constant with Frequency and Temperature

The dielectric response is generally described by the complex permittivity $\varepsilon^* = \varepsilon' - i \varepsilon''$, where ε' and ε" components are the storage and loss energy in each cycle of applied electric field. Figure 1 gives the dependence of dielectric permittivity ε' on the frequency of the applied field at room temperature for pure PMMA and PMMA doped with different contents of azo dye. The dielectric permittivity as a function of frequency (100 Hz – 100 KHz) reflects the

important effect of the azo dye content on the properties of pure PMMA. It is noticed that the values of ε' for the doped samples is higher than that in pure PMMA and increases with increasing the doping level at all the frequency range. Figure 2 Similar results were also observed by the number of researchers [9-11]. This can be attributed to either the enhanced mobility of the motion of polymer molecule or due to the rotation of the side acrylate group of the host polymer. This is caused due to a free volume enhancement offered by the large size of the dye molecule [12]. One further effect may contribute to the rise in permittivity, when the doping is done, the quantity of the accumulated charge will increase because the polarization of the polymer / dopant interfaces. The polarization makes an additional contribution to the charge quantity. From this point of view, the dielectric constant of the azo dye doped polymer will be higher than that of the pure polymer [13].

Figure 3 (a, b) shows the dependence of dielectric permittivity on frequency at room temperature at different UV- irradiation times for PMMA and PMMA doped with 1 wt% of azo dye as a representative for the azo dye content. It is observed that the UV-irradiation has no effect on ε' of pure PMMA and doped with azo dye.

Figure 4 (a-e) shows the variation of ε' with frequency at different temperatures for pure PMMA and PMMA doped with different contents of azo dye. It is evident from these figures that the behavior of all samples has the same trend. The values of the dielectric permittivity are high farther at low frequency and decrease monotonically with increasing frequency and attain a constant value at higher frequencies. Similar behavior was observed in a number of polymers [14-15]. Such high value of ε' may be due to the interfacial effects within the bulk of the sample and the electrode effects [16]. Verifying the fact that for polar materials the initial value of dielectric permittivity is high, but as the frequency of the field is raised, the value begins to drop which could be due to the fact that dipoles are not able to follow the field variations at high frequencies, and also due to electrode polarization effects [17]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of ε' [18,19]. As a result, the decrease in ε' can be explained by Jonscher's power low, i.e ε' α f n-1 where $0 < n < 1$ and it does not reveal any peak in the measured frequency range. Figure 5 (a-e) show the temperature dependence of the dielectric permittivity ε' in the frequency range 100 Hz to 100 K Hz for pure PMMA and PMMA doped with different contents of azo dye. The variation of ε' with temperature is different for polar and non-polar polymers. In general, for non-polar polymers the values of ε' are independent of temperature but in the case of strong polar polymers ε' increases as the temperature increases. However, since the specific volume of the polymer increases as the temperature increases, ε' decreases with increasing temperature in the case of weak polymers [20].

The increase in ε' with temperature up to Tg is due to greater freedom of movement of dipole molecular chain of polymer at high temperature. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the field cannot change the condition of dipoles. As the temperature increases, the dipoles comparatively become free and they respond to the applied electric field. Thus polarization increases and hence ε' increases with the increase of temperature. One further effect may contribute to the increase of ε' before Tg, the change in the intra and inter-molecular interactions may involve the alignment or rotation of the dipoles present in the polymer with the increase of temperature [21].

Variation of Loss Tangent Tan δ with Frequency and Temperature

The study of dielectric loss as a function of temperature and frequency was used to characterize the molecular motion and dielectric relaxation behavior of the polymer [22, 23].

PMMA, like any polymers, undergoes several structural transitions. Upon heating from low temperature, there is beta transition (glass-glass transition) and alpha transition (glass-rubber transition Tg). Typical result of dielectric loss tangent (tan δ) as a function of temperature at different frequencies for pure PMMA and PMMA doped with different contents of azo dye are shown in Figure 6 (a-e). From the plots, it is clear that tan δ values decrease with increasing the frequency. Also, it can be seen that all curves are characterized by a one tan δ peak in the region of glass transition Tg corresponding to the α-relaxation. The tan δ peak shifts to the high temperature side with the increase in the frequency. The α-relaxation peak is attributed to the rotation of lateral groups around main chain axis [24]. The α-relaxation peak which corresponds to the Tg in PMMA may be explained as the molecular mobility near Tg and mainly depends on the free volume [21]. In the glassy state, the free volume will remain at a constant value below Tg. The polymer will, however, expand with increasing temperature due to normal expansion process of all molecules, which result from the changing vibrational amplitudes of bond distances. About Tg, in addition to the normal expansion process, there will be an expansion of free volume itself, which will result in a large expansion of the rubber like polymer. This yields a sufficient place for molecular motion by a rotation or translation to occur. Due to this increase in chain segment mobility, there will be a large increase in tan δ at Tg. The observed peak is not symmetric, with a broadening towards the lower temperatures. This broadening is due to the β-relaxation, induced by the rotation of acrylate groups around the C-C bonds which link them to the main chain of the polymer [25]. It is noticed that for azo dye doped samples, the positions of α-relaxation peak is shifted significantly towards lower temperatures. This can be explained as follows: the increase of free volume by addition of azo dye leads to increasing the segmental mobility, and then the lower glass transition Tg [26]. The dielectric loss tangent tan δ as a function of temperature at frequency 100 Hz for pure PMMA and PMMA doped with azo dye is represented in Figure 7. From this figure we can obtain the Tg values of the present system (Table 1) The values of Tg decreases monotonically as the azo dye content increases. The Tg value of pure PMMA obtained from the loss peak agrees well with the Tg values obtained in literatures.

AC Conductivity

Beside the study of ε' and tan δ, AC conductivity of the present system was analyzed. The AC electrical conductivity σ_{AC} of PMMA and PMMA doped with azo dye as a function of frequency was studied in the frequency range 100 Hz – 100 KHz. From the measured capacitance and dielectric loss, σ_{AC} of the present system was calculated. Figure 8 shows the frequency dependence of the electrical conductivity for pure PMMA and PMMA doped with different contents of azo dye at room temperature. It is observed that the conductivity significantly increases with increasing the frequency and slightly increases with increasing the content of the azo dye. It is known that the conductivity of such composites depends on the type and concentration of the dispersed dopant, chain length, the orderness and molecular orientations in the material [27]. The orderness increases with increasing azo dye concentration, which is also responsible for increasing the conductivity. Figure 9 (a, b) give the dependence of σ_{AC} on the frequency for pure PMMA and PMMA doped with 1 wt% of azo dye (as a representative for the azo dye content) at different times of UV-irradiation. The results state that the UV-irradiation has no effect on σ_{AC} of pure PMMA and PMMA doped with azo dye. These results confirm the observation on the dielectric permittivity and refractive index study in the present work. The dependence of σ_{AC} on the frequency at different temperatures in the lower temperature side of α-relaxation process was considered. Figure 10 (a,b) shows the dependence of Log (σ_{AC}) on the frequency at temperature range 30-100°C for the present system. It can be observed from these figures that σ_{AC} for all investigated samples increases with increasing the temperature and the frequency.

It is known that the Ac conductivity of the amorphous materials depends on the measuring frequency according to:

$$\sigma_{AC} = A\omega^{S}$$

(3-1)

where A is a constant, ω is the angular frequency and s is the power of frequency. The frequency power s $\leq$ 1 (up to 1 MHz) [27]. The values of the s were obtained from the slopes of the straight lines for all investigated samples at different temperatures using the logarithmic form of equation (3 – 1). Such study was first reported by Jonscher [28] for a wide variety of materials, amorphous semiconductors and glasses [29]. In most cases, s is found to be between 0.5 and 0.7 for ionic conducting materials [30]. The value of S = 1 is regarded theoretically as the limiting value. The temperature dependence of the frequency power s gives information on the specific mechanism involved. Figure 11 shows the dependence of s on the temperature for films of pure PMMA and PMMA doped with azo dye. It can be observed that for pure PMMA the values of S are near unity at room temperature and then decreases with increasing the temperature. On the other hand for the doped samples, the values of s are lower than that of pure PMMA and decreases slightly at higher temperatures. The values of s is less than unity for all samples, i.e. 0 < S < 1.

The frequency and temperature dependence of Ac conduction in amorphous glasses and polymer materials can be interpreted using different models. Quantum mechanical tunneling (QMT) is the first model, which suggests that σ_{AC} increases linearly with increasing temperature. In this model the frequency power s is almost equal to 0.8 and increases slightly with increasing temperature or nearly independent of temperature. Our experimental results do not agree with this model.

CONCLUSIONS

In the present study the results demonstrate significant modification in the structure, optical and electrical properties in the PMMA films doped with azo dye. From these results, the following conclusions were drawn:

- The values of ε' decreases with increasing the frequency and attain a nearly constant value at high frequency. The values of ε' increase with azo dye doping due to the induced increase in free volume.

- $\varepsilon'(T)$ shows increase of dielectric constants with increasing the temperature up to the glass temperature. This can be interpreted as, the increase in temperature increases the orientation of molecules up to a maximum value near Tg.

- The results of tanδ (T) gives one relaxation peak due to α- relaxation process (Tg). The position of this peak for pure PMMA film is greater than that of doped films and decreases with increasing the doping level.

- σ_{Ac} (T) curves at different frequencies indicate that, below Tg σ_{AC} increases with increasing the frequency and temperature as well as azo dye content. For all investigated samples, at constant temperature, the frequency dependence of σ_{AC} is found to obey the relation $\sigma_{AC}=A\omega s$. The results show that the correlated barrier hopping mechanism (CBH) is the most suitable mechanism to describe the Ac conduction behavior in the present system in the frequency range 0.1-100 kHz and temperature range 30-100 °C.

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